PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PC-8911	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/JP 03/07619	International filing date *(day/month/year)* 16.06.2003	Priority date *(day/month/year)* 14.06.2002
International Patent Classification (IPC) or both national classification and IPC C09D4/00		
Applicant DAINIPPON INK & CHEMICALS, INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 12 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
02.02.2004	14.10.2004
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Clement, S Telephone No. +49 89 2399-8512

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/JP 03/07619

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

2-4, 6-9, 14-16, 19, 21	as originally filed
1, 5, 10-13, 17, 18, 20, 22	filed with telefax on 24.09.2004

Claims, Numbers

1-7	filed with telefax on 24.09.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-7
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-7
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-7
	No:	Claims	

2. Citations and explanations

see separate sheet

Ad Section V:

Novelty (Art. 33 (2) PCT)

EP-A-0 808 860 discloses a curable resin composition comprising
(a) a compound containing a plurality of ethylenic unsaturations between carbon atoms at α- and β-positions relative to a carbonyl group (e.g. polyester acrylate resins);
(b) an acrylate polymer containing a plurality of malonate-terminated pendant groups in the molecule and
(c) a catalyst capable of promoting the Michael reaction between (a) and (b).
As component (c) triphenylphosphine may be used. The strong base (c) may be blocked with a carboxylic acid which undergoes volatilization or decarboxylation under baking conditions (claims 1-3 and 7; page 4, lines 27-40). Moreover, a carboxylic acid may also be used as a constituent of the curable composition (Table 1).

In contrast to EP'860, the composition according to claims 1-7 uses an tertiary *alkyl* phosphine as component (c).

Neither EP-A-0 448 145 nor US-A-4 408 018 as cited in the international search report discloses the composition as claimed containing the tertiary alkyl phosphine (c).

Therefore, novelty over the cited prior art is given.

Inventive Step (Art. 33 (3) PCT)

EP'860 is considered to be the nearest prior art.

By a comparative example sbmitted by the Applicant in which triphenylphosphine is used instead of trioctylphosphine (Example 1 of the application), it has been demonstrated that the composition according to the invention exhibits improved properties concerning solvent resistance and pencil hardness of the cured products over the products according to EP'860.

As the EP'145 and US'018 do not mention component (c) at all, these documents do not add any information to the teaching of EP'860.

Thus, the present claims 1-7 involve an inventive step.

Industrial applicability (Art. 33 (4) PCT)

Present claims 1-7 fulfill the requirements of Art. 33 (4) PCT).

WO 03/106570

PCT/JP03/07619

DESCRIPTION

STORAGE STABLE CURABLE COMPOSITION

TECHNICAL FIELD

This invention relates to curable compositions, which are particularly usable for coatings, comprising compounds containing activated unsaturated groups, compounds containing activated hydrogen atoms, tertiary organic phosphines and carboxylic acids. The compositions can be cured at low temperatures and show at the same time good storage stability at room temperature.

BACKGROUND ART

Coating compositions containing activated unsaturated groups and activated hydrogen atoms are known, in general, from several references.

An early example is German Patent No. DE-PS 835809, which discloses a process for production of products derived from compounds containing activated hydrogen atoms, including activated methylene groups, and activated double bonds.

U.S. Patent No. 2,759,913 discloses a composition of the above type, which may be prepared at ambient and elevated temperatures. More specifically, the reference generally describes the production of polymeric materials prepared from compounds containing at least two activated ethylenic double bonds and components containing at least two activated

5,017,649, are more soluble in organic coatings, but they also reduce the hydrolytic stability of the coatings. This is known from Journal of Coatings Technology, Vol. 61, No. 770, March 1989, page 89. The sensitivity of polyesters towards hydrolysis in the presence of strong alkaline catalysts was also described in a product information bulletin from Eastman Kodak Company: "The Utility of Acetoacetoxyethyl Methacrylate (AAEM) in Thermoset Coatings" (page 14, last section: "Michael addition").

DISCLOSURE OF INVENTION

Therefore, the object of the present invention is to provide curable compositions, particularly usable for coatings, which can be crosslinked at low temperatures or room temperature but which are, on the other hand, also storage stable at room temperature, and which do not suffer from the drawbacks of strong basic catalysts, which may impart yellowing, cloudiness, and hydrolysis instability to the coating.

According to the invention, the object is achieved by the curable compositions of this invention which is:

A curable composition comprising:

(i) a compound (A) having at least two unsaturated groups which are activated for Michael addition,

(ii) a compound (B) having at least two activated hydrogen atoms,

(iii) a tertiary organic phosphine (C), and

liquid curable coating compositions, the number average molecular weight of the compound (B) having at least two activated hydrogen atoms should be preferably in the range between 230 and 2,000. For solid powder coating systems, the number average molecular weight of the compound (B) having at least two activated hydrogen atoms could be preferably in the range between 1,000 and 40,000.

Compounds containing both malonate and acetoacetate groups in the same molecule are also suitable and can be obtained, for example, by the Michael addition between a malonate functional polyester and an acetoacetate functional acrylic compound (e.g., acetoacetoxyethyl acrylate). Additionally, simple mixtures of malonate and acetoacetate group-containing compounds are suitable as well. Low molecular weight alkyl acetoacetates and malonates, such as ethyl acetoacetate and dimethyl malonate, may also be used as reactive diluents.

The compound (B), which includes the aforementioned and other malonate and/or acetoacetate group-containing compounds and their methods of production, are generally known to those skilled in the art.

The tertiary organic phosphine (C) may be aliphatic, cycloaliphatic, aromatic, or of mixed character.

Suitable examples include tributylphosphine, triisobutylphosphine, tri-tertiary-butylphosphine, tris(2,4,4-trimethylpentyl)phosphine, tricyclopentylphosphine, tricyclohexylphosphine, tri-n-octylphosphine (TOP), tri-n-

dodecylphosphine, trivinylphosphine, tribenzylphosphine, dimethylphenylphosphine, cyclohexyldiphenylphosphine, dicyclohexylphenylphosphine, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, triphenylphosphine (TPP), tertiary arylphosphines activated by electron donating groups -OR or $-NR_2$ (R = H, C_1-C_{12}-alkyl, C_1-C_{12}-aryl) such as diphenyl(2-methoxphenyl)phosphine, tris(4-methoxyphenyl) phosphine, tris(2,6-dimethoxyphenyl)phosphine, tris(4-dimethylaminophenyl) phosphine, and tertiary alkylphosphines containing phosphorous bound hetero atoms such as hexamethylene triaminophosphine and hexaethylene triaminophosphine.

Preferred among the above-exemplified tertiary organic phosphine (C) is a tertiary alkyl phosphine such as tributylphosphine, triisobutylphosphine, tri-tertiary-butylphosphine, tris(2,4,4-trimethylpentyl)phosphine, tricyclopentylphosphine, tricyclohexylphosphine, tri-n-octylphosphine (TOP), and tri-n-dodecylphosphine. In contrast to alipohatic tertiary phosphines, aromatic tertiary phosphines show very low catalytic activity, if any.

From the viewpoint of handling, safety, and environmental properties (e.g., a low vapor pressure), tri-n-octylphosphine (TOP) and tri-n-dodecylphosphine are particularly preferable.

The aforementioned phosphines are commercially available or may be prepared according to standard methods of organic chemistry such as Grignard reaction of alkylhalogenides with

phosphorous trichloride or catalytic addition of alkenes to phosphane.

The carboxylic acid (D) represents compounds containing carboxylic acid groups.

Various carboxylic acids can be used in the curable compositions of this invention, which carboxylic acids can extend the pot-life of the mixture considerably and make them storage stable at ambient temperature. Among these, some carboxylic acids are preferred for the curing at elevated temperatures above 100°C, such as formic acid, acetic acid, propionic acid, pentanoic acid, hexanoic acid, malonic acid, cyanoacetic acid, nitroacetic acid, phenylacetic acid, α-oxoacetic acid, acrylic acid, methacrylic acid, maleic acid, succinic acid, and glyoxylic acid.

Preferred among them is a saturated fatty acid having a molecular weight of 80 or less, such as formic acid, acetic acid, or propionic acid, especially for curing at low temperatures below 100°C or even at room temperature.

The curable compositions of this invention are prepared by blending, mixing, or dissolving the aforementioned compound (A), compound (B), tertiary organic phosphine (C), and carboxylic acid (D) at room temperature. Important is the sequence of the addition of compound (A), compound (B), tertiary organic phosphine (C), carboxylic acid (D). In general, carboxylic acid (D) must be present in a system which is able to react (both components A+B are present) before the addition of tertiary organic phosphine (C).

Thus, a preferable method for the preparation of the curable composition comprises mixing compound (A), compound (B), tertiary organic phosphine (C), and carboxylic acid (D) in an arbitrary order with the proviso that tertiary organic phosphine (C) is added after the addition of carboxylic acid (D).

In a further embodiment, the mixture of tertiary organic phosphine (C) and carboxylic acid (D) is prepared separately and the mixture is then mixed with compound (A) and compound (B) in an arbitrary order.

After the addition of each component, the mixture is thoroughly stirred in order to finely disperse or dissolve the components in each other before the addition of the next component is processed. As mentioned above, the addition of tertiary organic phosphine (C) to a solution of (A+B) before adding carboxylic acid (D) may result in an immediate increase in viscosity and formation of gel particles, so that the curable coating composition can no longer be applied. The amount of tertiary organic phosphine (C) is 0.1-10% by weight, preferably 0.2-2.0% by weight of the total weight of the curable coating composition.. The amount of carboxylic acid (D) depends on the amount of tertiary organic phosphine (C). The equivalent of the carboxylic acid groups of carboxylic acid (D) should exceed the equivalent of the phosphine compounds of tertiary organic phosphine (C). For good long term storage stability, the carboxylic acid group equivalent may be applied in an excess of at least 50%.

EXAMPLES:

Example 1

100 ml of toluene was sparged with nitrogen and heated to 90°C. Then, a solution of 60.0 g of methyl methacrylate, 20.0 g of butyl acrylate, 20.0 g of 2-acetoacetoxyethyl methacrylate, and 1.50 g of azobisisobutyronitril (AIBN) was dropped into hot toluene over 3 hours. Then, the mixture was stirred for another three hours. After cooling to room temperature a viscous resin was obtained containing a copolymer having pendant acetoacetate groups, which represents compound (B), (molecular number average: Mn = 16,000; glass transition temperature: Tg = 38°C). To that resin, 30.0 g of trimethylolpropane triacrylate (compound (A)) was added and dissolved followed by 0.7 g of formic acid (carboxylic acid (D)) and 2.0 g of trioctylphosphine (tertiary organic phosphine (C)).The mixture was adjusted with additional toluene until a coating viscosity of 200 mPas at 25°C was reached. The final curable coating composition was applied on top of an aluminum specimen at a coating thickness of approximately 40 µm and cured under two different conditions at 75°C for 30 minutes and at 120°C for 30 minutes.

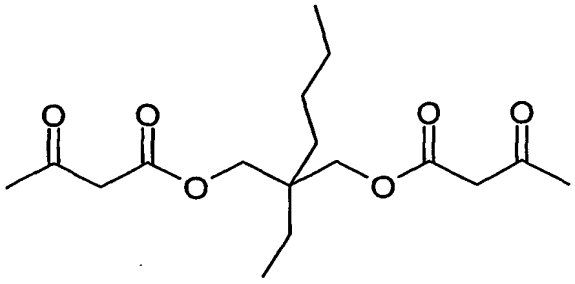
Solvent resistance[1] / Pencil hardness[2] (75°C/30 min)	Solvent resistance[1] / Pencil hardness[2] (120°C/30 min)	Storage Stability at Room Temp.
50 2H	>200 3H	> 6 months

[1]Solvent resistance of the hardened coating, tested by repeated rubbing of the film surface with a woodpulp cloth impregnated with methyl ethyl ketone (MEK). The number of rubbings that still did not produce any visible damage to the coating was measured.

[2]Pencil hardness (measured according to ASTM procedure D3363)

Examples 2-10

General procedure: 5.00 g of trimethylolpropane triacrylate (compound (A)) was mixed with 5.00 g of the diacetoacetate (compound (B)),



which was prepared by transesterification of ethyl acetoacetate and 2-butyl-2-ethyl-1,3-propane diol. To that mixture, 1.0 mmol of a carboxylic acid (carboxylic acid (D), see Table 1 below, column 3) was added and completely dissolved. Then, 0.5 mmol of a phosphine compound (tertiary organic phosphine (C), see Table 1 below, column 2) was added

Table 1:

Example	Tertiary organic phosphine (C)	Carboxylic acid (D)	Solvent resist.[1]/ Pencil hardness[2] (25°C/ 7 days)	Solvent resist.[1]/ Pencil hardness[2] (80°C/ 30 min)	Solvent resist.[1]/ Pencil hardness[2] (140°C/ 20 min)	Storage Stability at Room Temp.
2	TOP	Formic acid	25 H	30 2H	>50 2H	>6 months
3	TCHP	Acetic acid	15 H	30 2H	50 2H	4 months
4	TOP	Malonic acid	no cure	3 H	10 2H	>6 months
5	DCHPP	Formic acid	30 H	45 2H	>50 2H	>6 months
6	TOP	Acetic acid	15 6B	40 H	> 50 2H	3 months
7	TCHP	Malonic acid	no cure	2 HB	8 2H	6 months
8	TCHP	Formic acid	30 H	40 2H	> 50 2H	> 6 months
9	DCHPP	Acetic acid	15 H	35 2H	> 50 2H	3 months
10	TOP	Glyoxylic acid	no cure	39 H	>50 H	2 months

[1]Solvent resistance of the hardened coating, tested by repeated rubbing of the film surface with a woodpulp cloth impregnated with methyl ethyl ketone (MEK). The number of rubbings that still did not produce any visible damage to the coating was measured.

[2]Pencil hardness (measured according to ASTM procedure D3363)

TOP = trioctylphosphine

TCHP = tricyclohexylphosphine

DCHPP = dicyclohexylphenylphosphine

Examples 11-14

General procedure: 5.00 g of trimethylolpropane triacrylate (compound (A)) was mixed with 7.50 g of the oligomeric malonate depicted below (compound (B), molecular weight ~1,000),

Table 2:

Example	Tertiary organic phosphine (C)	carboxylic acid (D)	Solvent resist.[1]/ Pencil hardness[2] (100°C/30 min)	Solvent resist.[1]/ Pencil hardness[2] (145°C/20 min)	Storage Stability at Room Temp.
11	TOP	Formic acid	25 H-B	>50 H-2H	6 months
12	TOP	Acetic acid	20 3B	40 H	4 months
13	TOP	Malonic acid	3 3B	50 H-2H	6 months
14	TOP	Glyoxylic acid	20 H	~ 50 2H	3 months

[1]Solvent resistance of the hardened coating, tested by repeated rubbing of the film surface with a woodpulp cloth impregnated with methyl ethyl ketone (MEK). The number of rubbings that still did not produce any visible damage to the coating was measured.

[2]Pencil hardness (measured according to ASTM procedure D3363)

INDUSTRIAL APPLICABILITY

The products of this invention are useful as coating materials or as materials to make binder components in varnishes, adhesives, paints, and printing inks.

CLAIMS

1. A curable composition comprising:

(i) a compound (A) having at least two unsaturated groups which are activated for Michael addition,

(ii) a compound (B) having at least two activated hydrogen atoms,

(iii) a tertiary organic phosphine (C), and

(iv) a carboxylic acid (D).

2. A curable composition according to claim 1, wherein the molar ratio of the unsaturated groups from the compound (A) and the activated hydrogen atoms from the compound (B) (former:latter) is in a range from 4:1 to 1:4.

3. A curable composition according to claim 1, wherein the tertiary organic phosphine (C) is present in an amount of 0.1-10% by weight.

4. A curable composition according to claim 1, wherein the carboxylic acid (D) is present in an amount of 0.05-10% by weight.

5. A curable composition according to claim 1, wherein the carboxylic acid (D) is a saturated fatty acid having a molecular weight of 80 or less.

6. A curable composition according to claim 1, wherein the tertiary organic phosphine (C) is a tertiary alkyl phosphine.

7. A crosslinked coating obtained from the curable composition according to claims 1-6.